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# Interfacial reactions and diffusion path in partial transient liquid-phase bonding of $Si_3N_4$/Ti/Ni/Ti/$Si_3N_4$[①]

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**Abstract**: The interfacial reactions in partial transient liquid-phase bonding of $Si_3N_4$ ceramics with Ti/Ni/Ti interlayers were studied by means of scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray diffractometry (XRD). It was shown that the interfacial structure of $Si_3N_4$/TiN/$Ti_5Si_3$ + $Ti_5Si_4$ + $Ni_3Si$/(NiTi)/$Ni_3Ti$/Ni was formed after bonding. The activation energies for TiN layer and the mixed reaction layer of $Ti_5Si_3$ + $Ti_5Si_4$ + $Ni_3Si$ are 546.8 kJ/mol and 543.9 kJ/mol, respectively. The formation and transition processes of interface layer sequence in the joint were clarified by diffusion path. An important characteristic, which is different from the conventional brazing and solid-state diffusion bonding, has been found, i.e., during the partial transient liquid-phase bonding, not only the reaction layers which have formed grow, but also the diffusion path in the subsequent reaction changes because of the remarkable variation of the concentration on the metal side.

**Key words**: ceramic joining; transient liquid-phase bonding; interfacial reactions; diffusion
**Document code**: A

## 1 INTRODUCTION

Partial transient liquid-phase bonding (PTLP), which has the advantages of both brazing and solid-state diffusion bonding, is a new technology used for ceramic joining[1~3]. Recently, the authors have been studying the partial transient liquid-phase bonding of $Si_3N_4$/Ti/Ni/Ti/$Si_3N_4$ with the emphases on the migration behavior of the interface and the selection of the bonding parameters[4]. The interfacial reactions between metals and ceramics and the interface structures are both the key factors which determine the interfacial strength[5,6]. At the present, there are many reports on the interfacial reactions between Ag-Cu-Ti or Cu-Ti brazing alloys and $Si_3N_4$ ceramics, while there are much fewer reports on the interfacial reactions between other alloys and $Si_3N_4$. By means of SEM, EDS and XRD, the interfacial reactions and diffusion path in partial transient liquid-phase bonding of $Si_3N_4$/Ti/Ni/Ti/$Si_3N_4$ were analyzed and discussed in the present paper.

## 2 EXPERIMENTAL

Hot-pressure-sintered $Si_3N_4$ ceramics and Ni sheets (0.8 mm in thickness) and Ti sheets (20 μm in thickness) were bonded at 1 273~1 423 K for 0.9~7.2 ks. The preparation method of the

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joints was described in Ref. [4]. The micrographs of the interfaces and the elemental distributions were observed or analyzed by S-630 SEM, J. S. M. 6301F field emission SEM and EDS. After bending tests, the surfaces fractured along the interface between ceramics and reaction layer were analyzed by XRD so as to determine the phase components of the interfacial reaction products. For the smooth interfacial fractures, the reaction layers were removed by mechanical method layer by layer so as to determine the reaction layer sequence by means of XRD.

## 3 EXPERIMENTAL RESULTS

### 3.1 Micrographs and elemental distributions of interfaces

The backscatter electron image of interface and corresponding EDS profile for joint processed at 1 323 K for 3.6 ks are shown in Fig. 1. It can be seen that a Ti-rich layer with relatively deep color and $Si_3N_4$ form a compact interface, and a much thicker reaction layer with relatively shallow color neighbouring the Ti-rich layer contains Ti, Ni and Si, but the content of Ti is higher than those of Ni and Si. By further analyzing the N content using the EDS equipped on the J. S. M 6301F field emission SEM, it was found that the Ti-rich reaction layer contains much more nitrogen (~59.82% in mole) than the thicker reaction layer does (~11.17% in mole).

The SEM micrographic changes of cross section at the interface bonded at different temperatures for 3.6 ks are shown in Fig. 2. It is thus clear that the interface structure after bonding is $Si_3N_4$/reaction layer/NiTi/$Ni_3Ti$/Ni. The effect of increasing temperature on the growth of the interfacial reaction layer is similar to that of increasing time[4], but in view of the smoothness of the interface between the ceramics and the

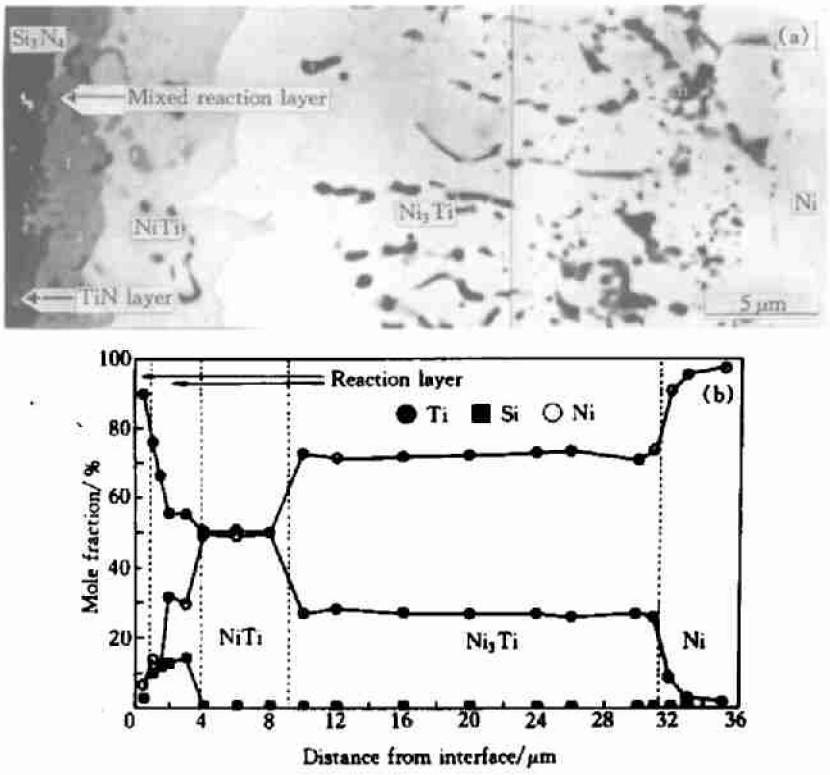


**Fig. 1** Backscatter electron image of interface (a) and corresponding EDS profile (b) for joint processed at 1 323 K for 3.6 ks

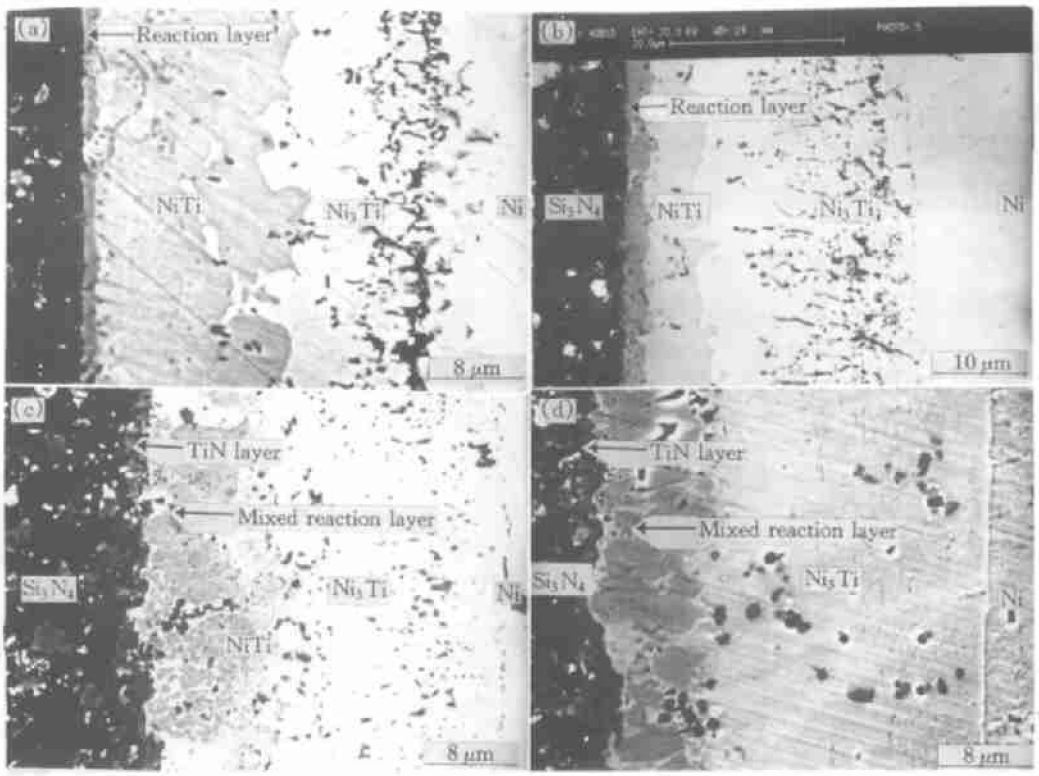


**Fig.2** SEM micrographic changes of cross section at interface bonded at temperature of (a) 1273 K, (b) 1323 K, (c) 1373 K and (d) 1423 K for 3.6 ks

reaction layer, the effect of temperature is more obvious[9].

### 3.2 XRD analyses

The bending samples bonded at 1323 K for 0.9 ks and 1.8 ks broke along the ceramics/intermediate layer interfaces. The fracture surface on the intermediate layer side is golden yellow, and its XRD pattern is presented in Fig. 3(a). The reaction products are TiN, $Ti_5Si_3$, $Ti_5Si_4$ and $Ni_3Si$. No above products were found on the fracture surface on the ceramics side, whose XRD pattern corresponds to that of the parent ceramics. This proves that the rupture occurs at the ceramics/reaction layer interface.

In order to clarify the interfacial reaction layer sequence, further XRD analyses after polishing were carried out (see Figs. 3(b) and (c)).

After part of the reaction layer had been polished (the fracture surface changes from golden yellow to shallow golden yellow), the intensities of the TiN spectral lines decrease, while those of the $Ti_5Si_3$, $Ti_5Si_4$ and $Ni_3Si$ spectral lines increase (Fig. 3(b)). After further polishing, the spectral lines of TiN disappear, the intensities of the $Ti_5Si_3$ spectral lines decrease obviously, but those of the $Ti_5Si_4$ and $Ni_3Si$ spectral lines further increase (Fig. 3(c)).

The above analyses indicate that the Ti-rich reaction layer neighbouring the $Si_3N_4$ ceramics is TiN, and the other reaction layer is a mixed layer of $Ti_5Si_3$, $Ti_5Si_4$ and $Ni_3Si$, and the possibility of $Ti_5Si_3$ neighbouring TiN is larger. The interface structure formed by partial transient liquid-phase bonding in this study is $Si_3N_4$/TiN/$Ti_5Si_3$ + $Ti_5Si_4$ + $Ni_3Si$/NiTi/$Ni_3Ti$/Ni.

### 3.3 Effects of bonding temperature and time on reaction layer thickness

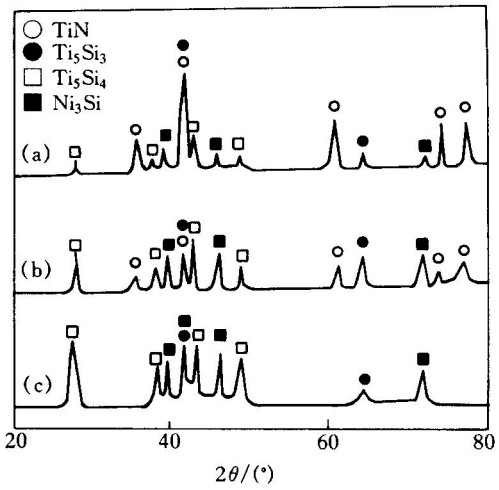


**Fig.3** XRD patterns of interface reaction layer heated at 1 323 K for 3.6 ks
(a)—Surface of reaction layer;
(b)—Part of reaction layer being polished;
(c)—After further polishing

When the bonding temperature is 1 323 K, the effects of the bonding time on the thickness of TiN layer and the mixed reaction layer are shown in Fig. 4. The growth of the reaction layer follows the parabolic rule and its thickness ($x$) can be described by

$$x = k\sqrt{Dt} \quad (1)$$

where $k$ is a material constant, $D$ is diffusion coefficient, and $t$ is bonding time.

At a definite bonding temperature, $D$ is a constant. Therefore Eqn. 1 can be simplified as

$$x = k_1\sqrt{t} \quad (2)$$

where $k_1$ is reaction layer growth coefficient.

Through regression treatment of the experimental data by means of the least square method, the reaction layer growth coefficients can be obtained:

$$k_1(\text{TiN layer}) = 1.3\times10^{-8}\ \text{m}\cdot\text{s}^{-1/2} \quad (3)$$

$$k_1(\text{Mixed layer}) = 7.4\times10^{-8}\ \text{m}\cdot\text{s}^{-1/2} \quad (4)$$

For a definite bonding time, the effect of bonding temperature on the reaction layer thickness can be described by

$$x = k\sqrt{D_0 t}[\exp(-Q/RT)]^{1/2} \quad (5)$$

or

$$\ln x^2 = -Q/RT + \ln K$$

where $Q$ is the activation energy for diffusion, $R$ is the universe gas constant, and $K$ is a constant.

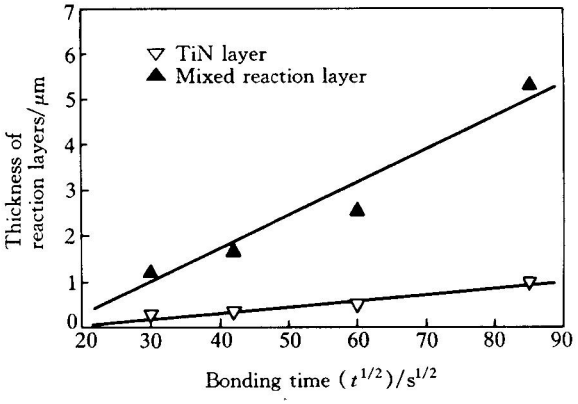


**Fig.4** Reaction layer thickness as a function of bonding time at a temperature of 1 323 K

The relation between the reaction layer thickness and the bonding temperature is presented in Fig. 5. The apparent activation energies for the growth of the TiN layer and the mixed layer, calculated from the slopes of the $\ln x^2$ vs $1/T$ straight lines, are estimated to be 546.8 kJ/mol and 543.9 kJ/mol, respectively.

## 4 DISCUSSION

### 4.1 Activation energy for growth of reaction layer

Assuming that the growth of the reaction layer is controlled by the diffusion of a kind of atom, then the apparent activation energy should be close to the diffusion activation energy of this atom in value. Nakao *et al* studied the brazing of $Si_3Ni_4$ ceramics by using Cu-5% Ti active brazing alloy, and obtained the reaction products of TiN and $Ti_5Si_3$. They calculated the activation energy for the growth of the reaction layer to be 318 kJ/mol, which is higher than that of the diffusion activation energy of N atoms diffusing in TiN (217.6 kJ/mol), thus concluding that the growth of the reaction layer is controlled by the diffusion of Ti atoms or Si atoms[10].

On the contrary, Naka *et al*[11] brazed the

ducing replacement reaction $4Ti + Si_3N_4 = 4TiN + 3Si$, the reaction layer will not continue to grow when the activity of Ti atoms reduces to a certain value[10]. The growth activation energy of the silicide reaction layer is very close to that of TiN, which shows that the growth of the silicide reaction layer is controlled by the above replacement reaction, i.e., by the diffusion of Ti crossing the reaction layer.

### 4.2 Diffusion path of interfacial reactions

In the temperature region that reactions can occur, some experiments verified that the TiN layer preferentially forms on the $Si_3N_4$ surface in the solid-state reaction between $Si_3N_4$ and Ti or Ti-containing alloys and in the interfacial reactions between $Si_3N_4$ and Ti-containing brazing alloys. The Si atoms released continue to react with Ti atoms to form different Ti-Si compounds, such as $Ti_5Si_3$[7,14,15], $Ti_5Si_3$ + $Ti_5Si_4$[4] and $TiSi_2$[16]. That biphase region forms in ternary diffusion couples conforms to the phase rule.

In the PTLP bonding of $Si_3N_4$ using the Ti/Ni/Ti intermediate layer in this work, because Ni also takes part in the reaction, i.e., $Si_3N_4$/Ti/Ni transforms into $Si_3N_4$/Ti-Ni(L)/Ni solid-liquid interface, the whole diffusion system contains a quarternary couple ($Si_3N_4$/Ti-Ni(L)/Ni) and a binary couple (Ti-Ni(L)/Ni). The transition processes of the interface layer sequence are analysed by diffusion path[17], as shown in Fig. 6.

Because the solid-state diffusion is very slow and the diffusion time is very short (above the eutectic temperature the Ti foils melt immediately), the interaction is very weak, and Ti atoms do not react with $Si_3N_4$. According to the Ti-Si-N ternary phase diagram and the diffusion path of the reaction between $Si_3N_4$ and Ti[18], there forms an interface structure of $Si_3N_4$/TiN/$Ti_5Si_3$(N)/Ti/Ti-Ni(L)/NiTi/$Ni_3Ti$/Ni (the solubility of N in $Ti_5Si_3$ is about 11% in mole), as shown in Fig. 6. The thickness of the reaction layer is very thin at this time.

After the complete melting of the Ti foils, the interface changes to $Si_3N_4$/TiN/$Ti_5Si_3$(N)/Ti-Ni(L)/NiTi/$Ni_3Ti$/Ni. At this time, Ti

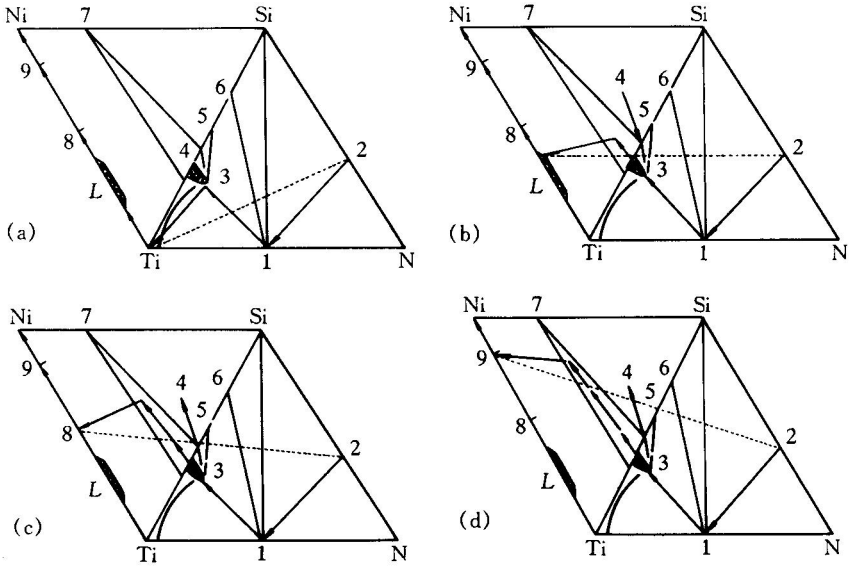


**Fig. 6** Diffusion path in partial transient liquid-phase bonding of $Si_3N_4$ with Ti/Ni/Ti multi-interlayers

1—TiN; 2—$Si_3N_4$; 3—$Ti_5Si_3$; 4—$Ti_5Si_4$; 5—TiSi; 6—$TiSi_2$; 7—$Ni_3Si$; 8—NiTi; 9—$Ni_3Ti$; *L*—Ti-Ni liquid

atoms rapidly cross the reaction layer and diffuse towards $Si_3N_4$, and continue to react with $Si_3N_4$ to thicken the reaction layer and form new reaction products. Because the diffusion path must cross the connecting line (the dash line) of $Si_3N_4$/Ti-Ni (L), there forms the interface structure of $Si_3N_4$/TiN/$Ti_5Si_3$ (N) + $Ti_5Si_4$ + $Ni_3Si$/Ti-Ni (L)/NiTi/$Ni_3Ti$/Ni, as shown in Fig.6(b).

When the Ti-Ni(L) layer is comsumed by the growth of the reaction layer and the NiTi layer (after isothermal solidification), the diffusion path along which Ni-Ti continues to react with $Si_3N_4$ is shown in Fig.6c. Compared with the second stage, the amount of the $Ni_3Si$ in the reaction products is increased, and the interface changes to $Si_3N_4$/TiN/$Ti_5Si_3$ (N) + $Ti_5Si_4$ + $Ni_3Si$/NiTi/$Ni_3Ti$/Ni.

At the fourth stage, after the NiTi layer has been consumed by the growth of the reaction layer and the $Ni_3Ti$ layer, the diffusion path is shown in Fig.6d, and the interface consists of $Si_3N_4$/TiN/$Ti_5Si_3$ (N) + $Ti_5Si_4$ + $Ni_3Si$/$Ni_3Ti$/Ni.

In the transition processes of the interface layer sequence, the diffusion and reaction of Ni obviously affect the concentration of the mixed reaction layer, which is reflected by the deviation of diffusion path towards the Ni-rich end. At the initial stage of reaction, there mainly form $Ti_5Si_3$(N) and a little $Ti_5Si_4$ neighbouring TiN layer, while at the final stage of reaction, the amount of $Ni_3Si$ obviously increases.

The changes of the diffusion path correspond well to the elemental distributions at the interface regions[4]. It can be concluded from the above analyses that an important characteristic of the interfacial reactions in partial transient liquid-phase bonding of ceramics/metal, which is different from the conventional brazing and the diffusion bonding, is that the homogenization of the liquid region and the isothermal solidification significantly change the concentration of the metal side, and as the reaction goes on, not only the as-formed reaction layer grows gradually, but also at the different stages of the interface reaction, the diffusion path of the continuous reaction will change.

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